



Result Page

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New Aryloxy (and/or. thio) aminopyrimidine

The present invention concerns new substituted Aryloxy (and/or. thio) aminopyrimidinderivate, their making, intermediate products to their preparation and their use as herbicides.

It is already well-known the fact that certain Diaminopyrimidinderivate possesses herbicides properties (see. R. Wegler ? chemistry of plant protection and pesticide? Bd. V, page 318-319, 1977). Furthermore it is well-known that determined Pyrimidyloxy (and/or. thio) phenylderivate (see. Show 9474/1967, DE-OS 3,442,077) herbicides effect.

Their effect is however under certain conditions, e.g. with low Aufwandmengen not always satisfying. Likewise the selectivity is not always sufficient.

Likewise it is well-known that certain 4-Aminopyrimidinderivate exhibits fungicidal properties (DE-OS 3,504,895).

Further monoaminosubstituierte pyrimidines show herbicides effects likewise (see. EP-A 1,187). Thus shows 2 (3-Chlorphenoxy) - 4-dimethylaminopyrimidin herbicides effect, which is however not always satisfying.

Now new Aryloxy became (and/or. thio) aminopyrimidine of the formula (I) found, EM12.1 in which

R< 1> for hydrogen, alkyl, Alkoxyalkyl, Cycloalkyl or alkenyl stands,

R< 2> for hydrogen or alkyl stands or

R< 1> and R< 2> together with the nitrogen atom, to which they are bound, also a three to sechsgliedrigen ring with 1 or 2 further heteroatoms to form know,

R< 3> for hydrogen or substituted alkyl stands if necessary,

X for oxygen or sulphur stands,

R< 4> and R< 6> independently for hydrogen, halogen, Nitro or for if necessary in each case substituted alkyl or Alkoxy stands and

R< 5> for hydrogen, halogen, Nitro, Hydroxy, in each case if necessary substituted alkyl, alkenyl or Alkynyl, in each case if necessary substituted Alkoxy, Alkoxyalkyloxy, Alkoxyalkoxyalkyloxy, Alkylthio, Alkylsulfoxy or alkyl sulphonyl, in each case if necessary substituted Alkylcarbonyl or Alkoxycarbonylalkyl stands or

R< 5> a remainder of the formula

- NR< 7> R< 8>

stands, how

R< 7> for hydrogen, if necessary substituted alkyl, for alkenyl or Alkynyl stands and

R< 8> for hydrogen, alkyl or a remainder of the formula

▲ top - @-R< 9>

stands, in which

B for oxygen or sulphur stands and

R< 9> for alkyl, alkenyl or Alkynyl stands, which if necessary by halogen, Nitro, Cyano, if necessary substituted aryl, and/or by one or more remainders of the formula

- C-R< 1> < 0>

substituted are, how

D for oxygen, sulphur, Sulfoxy or sulphonyl stands and

R< 1> < 0> for hydrogen, in each case if necessary substituted alkyl, alkenyl or aryl stand, or

R< 9> further for if necessary substituted Cycloalkyl or a if necessary substituted Heterocyclus stands,

R< 5> further for a remainder of the formulas EM14.1 stands how

R< 8> the meaning indicated above has and

R< 1> < 1> for if necessary substituted alkyl, for Alkoxyalkyl, alkenyl or Alkynyl stands,

R< 5> further for a remainder of the formula EM14.2 stands, how

n for the number of 1 or 2 stands and

R< 1> < 2> < - > < 1> , R< 1> < 2> < - > < 2> , R< 1> < 2> < - > < 3> and R< 1> < 2> < - > < 4> independently for hydrogen, halogen or alkyl stand,

R< 5> further for a remainder of the formula EM15.1 stands, how

E< 1> and E< 2> independently for oxygen or sulphur stand and

R< 1> < 3> < - > < 1> to R< 1> < 3> < - > < 7> independently for hydrogen or alkyl stand and m for the number of 1 or 2 stands.

Further it was found that one the Aryloxy (and/or. thio) aminopyrimidine of the formula (I) receives, if one

A) Pyrimidinderivate of the formula (II), EMI6.1 in which R< 1> , R< 2> and R< 3> the meaning indicated above have and

R< 1> < 4> for halogen or alkyl sulphonyl stands,

with (Thio) the formula (III) EMI6.2 in which phenolen

R< 4> , R< 5> , R< 6> and X the indicated meaning have,

if necessary in presence of a diluent and if necessary in presence of an acidic bonding agent converts, or

B) Halogenpyrimidinderivate of the general formula (IV) EMI7.1 in which

R< 3> , R< 4> , R< 5> and R< 6> it has the meaning indicated above under the condition that at least one of the remainders of R< 4> , R< 5> or R< 6> strong electron acceptor characteristic e.g. possesses like. Nitro or halogen alkyl and

Hal for halogen stands,

with an amine of the general formula (V) EMI7.2 in which

R< 1> and R< 2> the meaning indicated above have,

if necessary in presence of a diluent and if necessary in presence of an acidic bonding agent converts or

C-C1) Aryloxy (and/or. thio) aminopyrimidine of the formula (Ia) EMI8.1 in which

R< 1> , R< 2> , R< 3> , R< 4> , R< 6> and X the meaning indicated above have,

with reducing agents in presence of a diluent and in presence of a catalyst converts if necessary if necessary and

C-C2) the Aryloxy received after method C-C1 (and/or. thio) aminopyrimidine of the formula (Ib) EMI8.2 in which

R< 1> , R< 2> , R< 3> , R< 4> , R< 6> and X the meaning indicated above have,

alpha) with Säurehalogeniden of the formula (VI),

Hal-@-R< 9> (VI)

in which

R< 9> the meaning indicated above has and

Hal for halogen, in particular chlorine or bromine stands,

if necessary in presence of a diluent and if necessary in presence of an acidic bonding agent converts,

or

beta) with symmetric carbonic acid anhydrides of the general formula (VII),

R< 9> - @-O-@-R< 9> (VII)

in which

R< 9> the meaning indicated above has,

if necessary in presence of a diluent converts,

or

gamma) with asymmetric Säureanhydriden of the formula (VIII),

R-O-@-O-@-R< 9> (VIII)

in which

R< 9> the meaning indicated above has and

R for alkyl or alkyl sulphonyl with in each case 1 to 4 carbon atoms, Phenyl or Phenylsulfonyl stands,

if necessary in presence of a diluent converts,

or

delta) with omega - halogen carbonic acid halides of the formula (IX), EMI10.1 in which

R< 1> < 2> < - > < 1> , R< 1> < 2> < - > < 2> , R< 1> < 2> < - > < 3> , R< 1> < 2> < - > < 4> and n the meaning indicated above have and

Hal and Hal< 2> for halogen stand,

if necessary in presence of an acidic bonding agent and if necessary in presence of a diluent in a two-stage reaction sequence converts,

or

D) Aryloxy (and/or. thio) aminopyrimidine of the formula (IC) EMI11.1 in which

R< 1> , R< 2> , R< 3> , R< 4> , R< 6> and X the meaning indicated above have, and

R< 5> < - > < 1> for the remainder of EMI11.2 stands, whereby R< 7> and R< 9> the meaning indicated above have,

with sulfuration reagents, as for example phosphorus V sulfide or 2,4-Bis (4-methoxyphenyl) - 2,4-dithiono-1,2,3,4-

dithia-phosphetan (Lawesson reagent) converts EMI12.1 in which to connections of the formula (ID)

R< 1> , R< 2> , R< 3> , R< 4> , R< 6> and X the meaning indicated above have, and

R< 5> < - > < 2> for the remainder of EMI12.2 stands, whereby R< 7> and R< 9> the meaning indicated above have,

or

E) the connections (ID), manufactured after the method D), in those R< 7> for hydrogen stands, with connections of the formula (X)

L-R< 1> < 1> (X)

in which

R< 1> < 1> the meaning indicated above has and

L for halogen, Alkylsulfonyloxy or substituted Phenylsulfonyloxy stands if necessary,

with deprotonierenden bases and in presence of a diluent to connections of the general formula (IE) EMI13.1 in which

converts if necessary

R< 1> , R< 2> , R< 3> , R< 4> , R< 6> , R< 9> , R< 1> < 1> and X the meaning indicated above have,
or

F) Aryloxy (and/or. thio) aminopyrimidine of the formula (If) EMI13.2 in which

R< 1> , R< 2> , R< 3> , R< 4> , R< 6> and X the meaning indicated above have, and
R< 5> < - > < 3> for Hydroxy stands,
with connections of the general formula (XI),

R< 5> < - > < 4> - G (XI)

in which

R< 5> < - > < 4> for substituted alkyl, alkenyl, Alkoxyalkyl, Alkylthioalkyl or Alkylcarbonylalkyl or for a remainder of the formula EMI14.1 stands if necessary in each case, how

E< 1> , E< 2> , R< 1> < 3> < - > < 1> to R< 1> < 3> < - > < 7> and m the meaning indicated above have, and
G for halogen, Alkylsulfonyloxy or substituted Phenylsulfonyloxy stands if necessary,
in presence of a diluent and in presence of an acidic bonding agent converts if necessary.

Finally it was found that the new Aryloxy (and/or. thio) aminopyrimidine of the formula (I) by outstanding herbicides effect are characterised.

Surprisingly the Aryloxy according to invention possesses (and/or. thio) aminopyrimidine of the formula (I) substantially improves herbicides properties as the constitutionally most similar before-well-known materials. Thus the materials according to invention of the formula (I) let themselves be used substantially better for the weed control than e.g. 2 (3-Chlorphenoxy) - 4-dimethylaminopyrimidin (1 187/Beispiel admits 28) from EP-A, which are a structurally similar active substance.

The active substances according to invention are distinguished contrary to the before-well-known connections by a 4-Aminosubstituent in the Pyrimidinring and by the unsubstituierten positions indicated in the general formula (I) in the Pyrimidinring and aromatics.

The carbon chains in the individual remainders are straight-chain in each case or branch out. The substitution of the different remainders as for example the aliphatic, acyclischen or aromatic remainders can be simply in each case or multiple, directly or different.

Aryloxy are preferential (and/or. thio) aminopyrimidine of the formula (I) EMI15.1 in which

R< 1> for hydrogen, for alkyl with 1 to 6 carbon atoms, Alkoxyalkyl with 1 to 4 carbon atoms in the individual alkyl parts, Cycloalkyl with 3 to 6 carbon atoms or alkenyl with 3 to 6 carbon atoms stands,

R< 2> for hydrogen or alkyl with 1 to 6 carbon atoms stands or

R< 1> and R< 2> together with the nitrogen atom, to which they are bound, to form know a three to sechsgliedrigen ring, which contains 1 or 2 further heteroatoms if necessary such as oxygen and/or sulphur,

R< 3> for hydrogen or by halogen, C1-C6-Alkoxy and/or C1-C6-Alkylthio substituted alkyl with 1 to 6 carbon atoms stands if necessary,

X for oxygen or sulphur stands,

R< 4> and R< 6> independently for hydrogen, halogen, Nitro, if necessary by halogen if necessary stand for substituted alkyl with 1 to 6 carbon atoms or by halogen substituted Alkoxy with 1 to 6 carbon atoms and

R< 5> for hydrogen, halogen, Nitro, Hydroxy, if necessary by halogen, C1-C6-Alkoxy and/or C1-C6-Alkylthio substituted alkyl with 1 to 12 carbon atoms, if necessary by halogen substituted alkenyl with 2 to 12 carbon atoms, if necessary by halogen substituted Alkyl with 2 to 12 carbon atoms, in each case if necessary by halogen substituted Alkoxy,

Alkoxyalkyloxy, Alkoxyalkoxyalkyloxy, Alkylthio, Alkylsulfoxy or alkyl sulphonyl with in each case 1 to 12 carbon atoms in the individual alkyl parts, in each case if necessary by halogen, C1-C6-Alkoxy and/or C1-C6-Alkylthio substituted Alkylcarbonyl or Alkoxyalkyl with in each case 1 to 10 carbon atoms in the individual alkyl parts, for a remainder of the formula

- NR< 7> R< 8>

stands, how

R< 7> for hydrogen, if necessary by halogen substituted alkyl with 1 to 6 carbon atoms, alkenyl or Alkyl with in each case 3 to 6 carbon atoms stands and

R< 8> for hydrogen, alkyl with 1 to 10 carbon atoms, for a remainder of the formula

- @-R< 9>

stands, in which

B for oxygen of the sulphurs stands and

R< 9> for alkyl with 1 to 12 carbon atoms, alkenyl or Alkyl with in each case 2 to 12 carbon atoms stands, whereby alkyl, alkenyl and Alkyl substituted if necessary are by halogen, Nitro, Cyano, if necessary by halogen and/or halogeneous (C1-C4) - alkyl-substituted Phenyl and/or by or several, in particular to three, resembles or different remainders the formula

- D-R< 1> < 0>

in which

D for oxygen, sulphur, Sulfoxy or sulphonyl stands and

R< 1> < 0> for hydrogen, in each case if necessary by halogen and/or C1-C6-Alkoxy substituted alkyl with 1 to 6 carbon atoms or alkenyl with 2 to 5 carbon atoms, in each case if necessary by halogen, C1-C4-Alkyl and/or C1-C4-Alkoxy substituted Phenyl or Naphthyl stands, or

R< 9> further for if necessary by halogen, C1-C6-Alkyl, C1-C6-Alkoxy and/or Halogen-C1-C6-alkyl substituted Cycloalkyl with 3 to 8 carbon atoms or one if necessary by C1-C6-Alkyl and/or C1-C6-Alkoxy substituted Heterocyclus with 3 to 6 ring members and 1 or 2 oxygen and/or sulfur atoms stands, or
R< 5> further for a remainder of the formula EMI19.1 stands, in that
R< 9> the meaning indicated above has and
R< 1> < 1> for alkyl with 1 to 6 carbon atoms, for Alkoxyalkyl with 1 to 6 carbon atoms for each for alkyl part if necessary, substituted by halogen, for alkenyl or Alkynyl with in each case 3 to 6 carbon atoms stands, or
R< 5> for a remainder of the formula EMI19.2 stands, how
n for the number of 1 or 2 stands and
R< 1> < 2> < - > < 1> , R< 1> < 2> < - > < 2> , R< 1> < 2> < - > < 3> and R< 1> < 2> < - > < 4>
independently for hydrogen, halogen or alkyl with 1 to 6 carbon atoms stand, or
R< 5> for a remainder of the formula EMI20.1 stands, in which
E< 1> and E< 2> independently for oxygen or sulphur stand,
R< 1> < 3> < - > < 1> to R< 1> < 3> < - > < 7> independently for hydrogen or alkyl with 1 to 6 carbon atoms stand and
m for the number of 1 or 2 stands.

Connections of the formula (I) are particularly preferential, in which
R< 1> for hydrogen, alkyl or Alkoxyalkyl with in each case 1 to 4 carbon atoms in the individual alkyl parts, Cycloalkyl with 3 to 6 carbon atoms or alkenyl with 3 to 4 carbon atoms stands,
R< 2> for hydrogen or alkyl with 1 to 4 carbon atoms stands or
R< 1> and R< 2> together with the nitrogen atom, to which they are bound, for Aziridino, Pyrrolidino, Piperidino or Morpholino,
R< 3> for hydrogen or by halogen; C1-C4-Alkoxy and/or C1-C4-Alkylthio substituted alkyl with 1 to 4 carbon atoms stands if necessary,
X for oxygen or sulphur stands,
R< 4> and R< 6> independently for hydrogen, fluorines, chlorine, bromine, Nitro, if necessary by fluorines and/or chlorine substituted alkyl with 1 to 3 carbon atoms or if necessary by fluorines and/or chlorine substituted Alkoxy with 1 to 3 carbon atoms stand and
R< 5> for hydrogen, fluorine, chlorine, bromine, Nitro, Hydroxy, if necessary by halogen; C1-C4-Alkoxy and/or C1-C4-Alkylthio substituted alkyl with 1 to 10 carbon atoms, in each case if necessary by halogen substituted alkenyl or Alkynyl with in each case 2 to 9 carbon atoms, in each case if necessary by halogen substituted Alkoxy, Alkoxyalkyloxy, Alkoxyalkoxyalkyloxy, Alkylthio, Alkylsulfoxy or alkyl sulphonyl with in each case 1 to 10 carbon atoms, in each case if necessary by halogen, C1-C4-Alkoxy and/or C1-C4-Alkylthio substituted Alkylcarbonyl or Alkoxyalkonylalkyl with in each case 1 to 8 carbon atoms in the individual alkyl parts, for a remainder of the formula

- NR< 7> R< 8>

stands, how
R< 7> for hydrogen, alkyl with 1 to 4 carbon atoms, alkenyl or Alkynyl with in each case 3 to 4 carbon atoms stands and
R< 8> for hydrogen, alkyl with 1 to 8 carbon atoms, a remainder of the formula

- @-R< 9>

stands, in which
B for oxygen or sulphur stands and
R< 9> for alkyl with 1 to 9 carbon atoms, alkenyl or Alkynyl with in each case 2 to 9 carbon atoms stands, whereby alkyl, alkenyl and Alkynyl substituted if necessary are by halogen, Nitro, Cyano, if necessary by fluorine, chlorine, bromine and/or halogen - (C1-C3) - alkyl substituted Phenyl and/or by one, two or three equal or different remainders of the formula

- D-R< 1> < 0>

in which
D for oxygen, sulphur, Sulfoxy or sulphonyl stands and
R< 1> < 0> for hydrogen, in each case if necessary by halogen and/or C1-C4-Alkoxy substituted alkyl with 1 to 4 carbon atoms or alkenyl with 2 to 4 carbon atoms or by halogen, C1-C3-Alkyl and/or C1-C3-Alkoxy substituted Phenyl or Naphthyl stands if necessary in each case, or
R< 9> further for if necessary by halogen, C1-C5-Alkyl, C1-C5-Alkoxy and/or Halogen-C1-C3-alkyl substituted Cycloalkyl with 3 to 6 carbon atoms or one if necessary by C1-C4-Alkyl and/or C1-C4-Alkoxy substituted Heterocyclus with 3 to 6 ring members and with 1 or 2 oxygen and/or sulfur atoms, in particular for the Heterocyclus EMI23.1 stands and
R< 5> further for a remainder of the formula EMI23.2 stands, in that
R< 9> the meaning indicated above has and
R< 1> < 1> for if necessary by fluorines, chlorine and/or bromine substituted alkyl with 1 to 5 carbon atoms, Alkoxyalkyl with 1 to 4 carbon atoms for each alkyl part, for alkenyl or Alkynyl with in each case 3 to 4 carbon atoms stands, or
R< 5> for a remainder of the formula EMI24.1 stands, how
n for the number of 1 or 2 stands and
R< 1> < 2> < - > < 1> , R< 1> < 2> < - > < 2> , R< 1> < 2> < - > < 3> and R< 1> < 2> < - > < 4>
independently for hydrogen, fluorine, chlorine, bromine or alkyl with 1 to 4 carbon atoms stand, or
R< 5> for a remainder of the formula EMI24.2 stands, in which
E< 1> and E< 2> independently for oxygen or sulphur stand,
R< 1> < 3> < - > < 1> to R< 1> < 3> < - > < 7> independently for hydrogen or alkyl with 1 to 4 carbon atoms stand and

m for the number of 1 or 2 stands.

The connections of the formula (I) are completely particularly preferential, in which

R< 1> for hydrogen, methyl, ethyl, n-Propyl, i-Propyl, t-Butyl, Methoxyethyl, Ethoxyethyl, Cyclopropyl or allyl stands and

R< 2> for hydrogen, methyl, ethyl, n-Propyl or i-Propyl stands,

R< 1> and R< 2> together with the nitrogen atom, to which they are bound, for Aziridino, Pyrrolidino, Piperidino or Morpholino stands,

R< 3> for hydrogen or by fluorines, chlorine, Methoxy, Ethoxy, n-Propoxy, i-Propoxy, Methylthio and/or Ethylthio substituted alkyl with 1 to 3 carbon atoms stands if necessary,

X for oxygen or sulphur stands,

R< 4> and R< 6> independently for hydrogen, fluorines, chlorine, Nitro, in each case if necessary by fluorines and/or chlorine substituted methyl or ethyl, for if necessary in each case by fluorines and/or chlorine substituted Methoxy or Ethoxy stand and

R< 5> for hydrogen, fluorine, chlorine, Nitro, Hydroxy, if necessary by fluorines, chlorine, Methoxy, Ethoxy, n-Propoxy, i-Propoxy, Methylthio and/or Ethylthio substituted alkyl with 1 to 9 carbon atoms, in each case if necessary by fluorines and/or chlorine substituted allyl or Propargyl, in each case if necessary by fluorines and/or chlorine substituted Alkoxy, Alkoxyalkoxy, Alkoxyalkoxyalkoxy, Alkylthio, Alkylsulfoxy or alkyl sulphonyl with in each case 1 to 9 carbon atoms, in each case if necessary by fluorines, chlorine, Methoxy, Ethoxy, Methylthio and/or Ethylthio substituted Alkylcarbonyl or Alkoxycarbonyl with in each case 1 to 6 carbon atoms in the eizelnen alkyl parts, for a remainder of the formula

- NR< 7> R< 8>

stands, how

R< 7> for hydrogen, methyl, ethyl, allyl or Propargyl stands and

R< 8> for hydrogen, alkyl with 1 to 6 carbon atoms, a remainder of the formula

- @-R< 9>

stands, in which

B for oxygen or sulphur stands and

R< 9> for if necessary in each case by fluorines, chlorine, bromine, iodine, Cyano, if necessary by fluorines, chlorine and/or halogen - (C1-C2) - alkyl, whereby halogen stands in particular for fluorines and/or chlorine, substituted Phenyl and/or by one, two or three equal or different remainders to the formula

- D-R< 1> < 0>

substituted alkyl with 1 to 6 carbon atoms, alkenyl with 2 to 6 carbon atoms or Alkynyl with 2 to 6 carbon atoms stands, how

D for oxygen, sulphur, Sulfoxy or-sulphonyl stands and

R< 1> < 0> for hydrogen, in each case if necessary by fluorines, chlorine, bromine and/or C1-C4-Alkoxy substituted alkyl with 1 to 4 carbon atoms or alkenyl with 2 to 4 carbon atoms or by fluorines, chlorine, C1-C3-Alkyl and/or C1-C3-Alkoxy substituted Phenyl stands if necessary, or

R< 9> further for a cycloalkyl residue with 3 to 6 carbon atoms stands, who is substituted by fluorines, chlorine, C1-C3-Alkyl, C1-C3-Alkoxy and/or tri fluorine methyl if necessary, or for one by C1-C4-Alkyl or C1-C4-Alkoxy substituted satisfied 1 or 2 oxygen or sulfur atoms containing heterocyclic ring with 3 to 6 ring members, in particular for the Heterocyclus EMI28.1 stands if necessary, and

R< 5> further for a remainder of the formula EMI28.2 stands, in that

R< 9> the meaning indicated above has and

R< 1> < 1> for methyl, ethyl or Isopropyl, for Methoxymethyl, Methoxyethyl, Ethoxymethyl, Ethoxyethyl, allyl or Propargyl stands, or

R< 5> further for a remainder of the formula EMI28.3 stands, how

n for the number of 1 or 2 stands and

R< 1> < 2> < - > < 1> to R< 1> < 2> < - > < 4> independently for hydrogen, fluorine, chlorine, methyl, ethyl, n-Propyl or i-Propyl stand, or

R< 5> further for a remainder of the formula EMI29.1 stands, in which

E< 1> and E< 2> independently for oxygen or sulphur stand,

R< 1> < 3> < - > < 1> to R< 1> < 3> < - > < 7> independently for hydrogen, methyl or ethyl stand and m for the number of 1 or 2 stands.

Completely particularly to emphasize the group of connections of the formula (I) is, in which X for sulphurs stands and which those prefers remaining substituent above as completely particularly indicated meaning has.

If one uses (A) 4-Amino-6-methyl-2-methylsulfonylpyrimidin and p-Methylthiophenol in accordance with methods as basic materials, then the process of the method according to invention (A) can be shown by the following formula pattern: EMI30.1

If one uses ammonia in accordance with method (B) 4-Chlor-6-methyl-2 (4-nitrophenylthio) pyrimidin and as basic materials, then the process of the method according to invention can be shown by the following formula pattern: EMI30.2

Uses one in accordance with method (C-C1) 4-Amino-6-methyl-2 (4-nitrophenylthio) pyrimidin and hydrogen as starting materials in such a way can the process of the method according to invention by the following formula pattern be shown: EMI31.1

If one uses 4-Amino-6-methyl-2 (4-aminophenylthio) in accordance with method (C-C2/Variante alpha) pyrimidin and

acetyl chloride as basic materials, then the process of the method according to invention is shown by the following formula pattern: EMI31.2

If one uses 4-Amino-6-methyl-2 (4-aminophenylthio) in accordance with method (C-C2/Variante beta) pyrimidin and ISO butter acidic anhydride as basic materials, then the process of the method according to invention can be shown by the following formula pattern: EMI32.1

If one uses Pivaloylkohlensäureethylesteranhydrid in accordance with method (C-C2/Variante gamma) 4-Amino-6-methyl-2 (4-aminophenylthio) pyrimidin and as basic materials, then the process of the method according to invention can be shown by the following formula pattern: EMI32.2

If one uses 4-Amino-6-methyl-2 (4-aminophenylthio) in accordance with method (C-C2/Variante delta) pyrimidin and 4-Chlor-2,2-dimethyl-butansäurechlorid as basic materials, then the process of the method according to invention can be shown by the following formula pattern: EMI33.1

If one uses Lawesson reagent in accordance with method (D) 4-Dimethylamino-6-methyl-2 (4-t-butylcarbonylaminophenylthio) pyrimidin and as basic materials, then the process of the method according to invention is described by the following pattern: EMI33.2

If one uses Methylodid in accordance with method (E) 4-Dimethylamino-6-methyl-2 (4-t-butylthiocarbonylaminophenylthio) pyrimidin and as output materials, then the process of the method according to invention is described by the following pattern: EMI34.1

If one uses 4-Dimethylamino-6-methyl-2 (4-hydroxyphenylthio) in accordance with method (F) pyrimidin and 2-Methyl-2-methoxy-1-propyl-tosylat as basic materials, then the process of the method according to invention can be shown by the following formula pattern: EMI34.2

The Pyrimidinderivate of the formula (II), used with the method according to invention (A), are well-known or can after well-known methods of organic chemistry be received (see. A. Weissberger: The Chemistry OF heterocyclic compounds; The Pyrimidines, 1962 Interscience, New York).

In this formula (II) the remainders of R< stand; 1> , R< 2> , R< 3> preferably for those remainders, preferably which were already mentioned in connection with the description of the materials according to invention of the general formula (I). The remainder of R< 1> < 4> stands preferentially for chlorine, fluorine and methyl sulphonyl.

The phenols likewise used with this method and/or. Thiophenole are described by the general formula (III). In it the remainders of R< stand; 4> , R< 5> , R< 6> and X for the remainders, those already with the description of bonds of the formula (I) as prefers and/or. were particularly preferentially mentioned. The connections of the formula (III) are partly admit (see. DE-OS 2,156,345). They are new and already partly subject-matter of a parallel submitted application and subject-matter of this application.

Again and subject-matter of this application are the Thiophenole of the formula (IIIa) EMI35.1 in which R< 4> and R< 6> independently for hydrogen, halogen, Nitro or for if necessary in each case substituted alkyl or Alkoxy stands and

R< 5> < - > < 5> for if necessary substituted alkyl with at least a tertiary carbon atom it stands, under the condition that R< 5> < - > < 5> not for third. - Stands for Butyl, if R< 4> and R< 6> simultaneous for hydrogen stand.

The connections of the formula (IIIa) are preferential, in which R< 4> and R< 6> independently for hydrogen, halogen, if necessary by halogen if necessary stand for substituted alkyl with 1 to 6 carbon atoms or by halogen substituted Alkoxy with 1 to 6 carbon atoms and R< 5> < - > < 5> for alkyl with 5 to 12 carbon atoms with at least a tertiary carbon atom stands, which can be substituted by halogen, C1-C6-Alkoxy and/or C1-C6-Alkylthio.

The connections of the formula (IIIa) are particularly preferential, in which R< 4> and R< 6> independently for hydrogen, fluorines, chlorine, if necessary by fluorines and/or chlorine substituted alkyl with 1 to 3 carbon atoms or if necessary by fluorines and/or chlorine substituted Alkoxy with 1 to 3 carbon atoms stand and

R< 5> < - > < 5> for if necessary in each case by halogen, C1-C4-Alkoxy and/or C1-C4-Alkylthio substituted third. - Butylethyl or third. - Stands for Butylpropyl.

In particular R< stands; 5> < - > < 5> in formula (IIIa) for - CH₂-CH₂-C (CH₃)₃ or - CH₂-CH₂-CH₂-C (CH₃)₃.

In particular the connections EMI37.1 are mentioned.

The bonds of the formula (III) can be manufactured after well-known in principle methods.

Thus one receives for example (Thio), in those R< to phenol of the formula (III); 5> for an electron-attractive group stands, if one halogen benzene of the formula (XIIIa) EMI37.2 in which

R< 4> and R< 6> the meaning indicated above have and

R< 5> < - > < 6> for Nitro, Vinyl, if necessary substituted Alkylcarbonyl, Alkylsulfoxy or alkyl sulphonyl stands and Hal< 1> for halogen, in particular for fluorines, chlorine or bromine, stands, with alkali metal disulphides, in particular sodium disulphide, to which 2,156,345 procedural conditions described in DE-OS converts.

One receives the new-Thiophenole of the formula (IIIa) for example, if one connections of the formula (IIIb) EMI38.1 in which

R< 4> and R< 6> the meaning indicated above have and

R< 5> < - > < 7> for if necessary substituted alkyl with at least a tertiary carbon atom stands, with reducing agents as for example sodium boron hydride in presence of a diluent as for example Diethyleneglykoldimethylether at temperatures between 20 DEG C and 140 DEG C converts (see. Manufacture examples).

The connections of the formula (IIIb) fall under the formula (III) and are there described. R< 5> < - > < 7> in formula

(IIIb) preferably stands for alkyl with 4 to 11 carbon atoms with at least a tertiary carbon atom, which can be substituted by halogen, C1-C6-Alkoxy and/or C1-C6-Alkylthio. Particularly preferentially R< stands; 5> < - > < 7> for third. - Butylmethyl or third. - Butylethyl, which can be substituted by halogen, C1-C4-Alkoxy and/or C1-C4-Alkylthio.

Further one receives connections of the formula (IIb), if one halogen benzene of the formula (XIIIb) EMI39.1 in which R< 4> , R< 5> < - > < 7> and R< 6> the meaning indicated above have and Hal< 2> for halogen, in particular fluorine, chlorine or bromine stands, with Natriumhydrogensulfid in presence of a diluent as for example converts N-Methylpyrrolidon at temperatures between 50 DEG C and 200 DEG C (see. Manufacture examples).

The halogen benzene of the formula (XIIIa) and (XIIIb) fall under the general formula (XIII) and are there more near described. In the formula (XIIIa) R< stands; 5> < - > < 6> preferably for Nitro, if necessary by halogen, C1-C6-Alkoxy and/or C1-C6-Alkylthio substituted Alkylcarbonyl with 1 to 10 carbon atoms, Alkylsulfoxy or alkyl sulphonyl with in each case 1 to 12 carbon atoms. In the formula (XIIIb) R< has; 5> < - > < 7> preferably and/or. particularly prefers above with the description of the fabrics of the formula (IIIa) for this substituent preferred and/or. particularly indicated meaning prefers.

As acidic bonding agents all can be used usually for such conversions usable acidic acceptors with the lead-through of the method (A). Are preferably usable alkaline-earth oxides, alkali and alkaline-earth hydroxides and - carbonates, like sodium hydroxide, potassium hydroxide, calcium oxide, sodium carbonate and potassium carbonate, furthermore alkali alcoholates, - amides and - hydrides, like e.g. Natriummethylat, Natriumethylat, potassium third. - butylat, sodium amide and sodium hydride.

As diluents all usual inert organic Solventien can be used with the lead-through of the method (A). Preferably infrage comes hydrocarbons, like benzine, toluol and xylene, furthermore ether, like Dioxan, Glykoldimethylether and Diglykoldimethylether, in addition nitriles, like acetonitrile, and also strongly polar Solventien, like Dimethylsulfoxid, N-Methylpyrrolidon, sulfolane and dimethyl formamide.

The reaction temperatures can be varied with the lead-through of the method (A) within a larger range. Generally one works at temperatures between 0 DEG C and 200 DEG C, preferably between 50 DEG C and 150 DEG C.

The conversion after the method (A) is made generally under normal print.

With the lead-through of the method (A) one sets the basic materials of the formulas (II) and (III) in general mine in approximate äquimolaren quantities over. It is however also possible to use or other component in a larger surplus. The working-up takes place after usual methods.

The Halogenpyrimidinderivate used with the method according to invention (B) are partial well-known or can be received after well-known methods. They are defined by the formula (IV) general. In the formula (IV) the remainders of R< stand; 3> , R< 4> , R< 5> and R< 6> preferred or particularly it prefers for the meanings, which was already mentioned with the description of the materials according to invention of the general formula (I) for these remainders, under the condition that at least one of the remainders of R< 4> , R< 5> or R< 6> strong electron acceptor characteristics possesses like e.g. Nitro or halogen alkyl. Hal preferably stands for fluorines, chlorine or bromine.

The connections of the general formula (IV) are received, by one in a first reaction step (stage 1) Thiopyrimidinderivate of the general formula (XII) EMI42.1 in which R< 3> the meaning indicated above has, with halogen benzene of the general formula (XIII) EMI42.2 in which R< 4> , R< 5> and R< 6> the meaning indicated above have and Hal< 1> for halogen, in particular for fluorines, chlorine or bromine stands, if necessary in presence of a diluent and if necessary in presence of an acidic bonding agent converts, to connections of the general formula (XIV) EMI42.3 in which R< 3> , R< 4> , R< 5> and R< 6> the meaning indicated above have.

The connections of the general formula (XIV) become in a second reaction step with Halogenierungsmitteln such as Phosphoroxychlorid, phosphorus V chloride, thionyl chloride or phosgene into the connections of the general formula (IV) EMI43.1 in the R< 3> , R< 4> , R< 5> , R< 6> and Hal the meaning indicated above transferred.

The Thiopyrimidine of the general formula (XII) is well-known connections (S. for this A. Weissberger, The Pyrimidines Bd. I, S. 272, Wiley Interscience (1962)).

In formula (XII) the remainder of R< stands; 3> preferred and/or. particularly preferentially for the meaning, those already with the description of the fabrics according to invention (I) as prefers and/or. particularly preferentially for this remainder one mentioned.

The halogen benzene of the general formula (XIII) in the R< 4> , R< 5> and R< 6> the same meaning, those have with the description of the connections of the general formula (IV) indicated and also with the description of the fabrics according to invention of the general formula (I) as were already preferred and/or. were particularly preferentially defined, are well-known or can after well-known methods be received.

The Halogenierungsmittel used with the second Verfahrensstufe is well-known connections. Exemplarily are mentioned Phosphoroxychlorid, thionyl chloride, phosphorus V chloride or phosgene (see. for this: A. Weissberger, The Pyrimidines Bd. I, S. 162-168, Wiley Interscience (1962)).

With the lead-through of the method according to invention (1. Stage) to the making of the connections of the formula (IV) assigned Pyrimidinderivate of the formula (XII) and the halogen benzene derivatives of the general formula (XIII) are used generally approximate in equivalent quantities. It is however also possible to begin or other component in a larger surplus.

As acidic bonding agents strong bases become such as alkali metal or alkaline earth metal hydroxides or - alcoholates uses. The acidic bonding agent is used at least in duplicate equivalent quantity, related to the assigned Thiopyrimidin.

(XII).

As diluents insbesondere strong polar Solventien is suitable such as Dimethylsulfoxid, sulfolane, N-Methylpyrrolidon or dimethylformamide.

The reaction is accomplished at temperatures between 50 and 200 DEG C, preferably between 75 and 150 DEG C.

The Pyrimidinderivate of the general formula (XIV), used with the lead-through of the second reaction step, and the Halogenierungsmittel generally in equivalent quantities are used. Preferably the Halogenierungsmittel is used in the surplus.

The 2. Stage of the method can be accomplished in on or absence of a diluent. As diluents also the assigned Halogenierungsmittel can be used such as thionyl chloride or Phosphoroxychlorid in a suitable surplus. Likewise all Solventien inert against halogenierende Agentien is possible as diluents. Preferably usable hydrocarbons are such as benzine, benzene, toluol, xylene, tetralin, halogen hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, Chlorbenzol, o-Dichlorbenzol, beyond that ethers such as diethyl ethers, tetrahydrofurans and Dioxan.

The second reaction step to the making of connections of the formula (IV) is accomplished at temperatures between 0 and 150 DEG C, preferably between 50 and 125 DEG C.

As catalysts are preferred, N, N-Dimethylanilin and dimethylformamides are used.

The amines of the general formula (V), needed with the method according to invention (B), are well-known connections of organic chemistry. In the formula (V) the remainders have R< 1> and R< 2> preferred and/or. particularly prefers the meaning, those already with the description of the fabrics of the general formula (I) preferentially and/or. were particularly preferentially called.

As diluents (B) all usual organic Solventien and water can be used with the method according to invention.

Preferably one uses hydrocarbons such as benzine, benzene, toluol, xylene, tetralin, furthermore halogen hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, Chlorbenzol, o-Dichlorbenzol, in addition vinyl ketones such as acetone and Methylisopropylketon, further ethers such as diethyl ethers, tetrahydrofurans and Dioxan, beyond that esters of carboxylic acid such as ethyl acetate and also strongly polar Solventien such as Dimethylsulfoxid or sulfolane.

The reaction temperatures can be varied within a broad range. One converts the materials generally at temperatures between 0 and 300 DEG C, preferably between 50 and 150 DEG C.

The pressure can be varied with the method according to invention (B) within broad ranges. Generally one works at a pressure preferentially from 1 to 100 at., at a pressure from 1 to 20 at.

As acidic bonding agents all usual acidic acceptors are possible during the conversion to the method according to invention (B).

Tertiary amines are preferably usable such as tri-ethylamine, Pyridin and N, N-Dimethylanilin, furthermore alkaline earth metal oxides such as calcium oxide, carbonates such as sodium carbonate, potassium carbonate and calcium carbonate. Likewise it is possible to use the respective connections of the formula (V) as acidic bonding agents. The connection concerned must be used then at least in such quantity that the freed hydrogen halide is bound.

With the lead-through of the method according to invention (B) the basic materials of the general formulas (IV) generally become and (V) in equivalent quantities used, preferably uses one per mol of Halogenpyrimidinderivat of the formula (IV) 1.2 to 20 mol at amine component of the formula (V).

The working-up takes place after usual methods.

When reducing agents come with the method (C-C1) everything those materials infrage, who are usually used to the reducing aromatic nitro compounds. Elementary metals, like iron, are preferably usable zinc and tin, furthermore metal compounds in low Wertigkeitsstufen, like iron (II) - and tin (II) - salts, and in addition nonmetal connections in low Wertigkeitsstufen, like e.g. Salts of the hydrogen sulphide, alkali sulfites and alkali dithionites. In all other respects the reducing can also by catalytic hydrogenation with hydrogen in presence of a catalyst, like e.g. Raney nickel, take place.

As diluents all usual organic Solventien suitable for such reducing comes into consideration with the method (C-C1).

The reaction temperatures can be varied with method C-C1) within a larger range. They correspond to the temperatures, which are used with analog reactions. Generally one works at temperatures between 0 and 150 DEG C, preferably between 10 and 100 DEG C.

The lead-through of the reduction after the method (C-C1) and the working-up of the resulting reaction mixture take place after usual methods.

The Aryloxy necessary for the lead-through of the method according to invention (C-C2) (and/or. thio) aminopyrimidine of the formula (Ib) are available bonds according to invention and after method (C-C1).

In this formula the remainders of R< stand; 1> , R< 2> , R< 3> , R< 4> , R< 6> and X preferably and/or. particularly preferentially for the meanings, those already with the description of the fabrics according to invention of the formula (I) prefers and/or. particularly preferentially for these remainders were called.

~~As reaction components the further necessary Säurehalogenide (method C-C2/Variante-alpha) are clearly defined by the~~ formula (VI). In this formula R< has; 9> preferably that meaning, preferably which was already called in connection with the description of the materials according to invention of the formula (I) for this remainder. Hal preferably stands for fluorines, chlorine or bromine.

The Säurehalogenide of the formula (VI) are admitted or can after well-known in principle methods in simple way be manufactured.

As acidic bonding agents all usual acidic acceptors come into consideration during the conversion to the method according to invention (C-C2/Variante alpha). Tertiary amines, like tri-ethylamine, are preferably usable Pyridin and N, N-Dimethyl-aniline, furthermore alkaline earth metal oxides, like calcium oxide, alkali and alkaline-earth carbonates, like sodium carbonate, potassium carbonate and calcium carbonate. It is also possible to use the respective connections of the formula (Ib) for simultaneous as acidic bonding agents. In addition the connection concerned must be used then at least in such quantity that the freed hydrogen halide can be bound.

As diluents with the method according to invention (C-C2/Variante alpha inert opposite Säurehalogeniden) all Solventien to be used. Preferably usable hydrocarbons, like benzine, are benzene, toluol, xylene and tetralin, furthermore halogen hydrocarbons, like dichloromethane, chloroform, carbon tetrachloride, Chlorbenzol and o-Dichlorbenzol, in addition vinyl ketones, like acetone and methyl isopropylketon, further ethers, like diethyl ethers, tetrahydrofurans and Dioxan, beyond that esters of carboxylic acid, like ethyl acetate, and also strongly polar Solventien, like Dimethylsulfoxid and sulfolane. If the hydrolysis stability of the Säurehalogenids permits it, the conversion can be accomplished also in presence of water.

With the lead-through of the method according to invention (C-C2) alpha /Variante) becomes the basic materials of the formulas (Ib) and (generally VI) in approximated equivalent quantities uses. It is however also possible to begin or other component in a larger surplus. The working-up takes place thereafter after usual methods. Generally one proceeds in such a way that one removes failed salts and restricts the remaining reaction mixture by taking the diluent off. If one works in presence of water or of Solventien mixable with water, then one can proceed also in such a way that one dilutes the reaction mixture with water, which sucks developing mixture off or with a water little mixable organic solvents extracted, which wash, restrict organic phase and subject the remaining residue if necessary usual cleaning methods.

The reaction temperatures can be varied with the lead-through of the method according to invention (C-C2/Variante alpha) within a larger range. If one works in presence of a diluent and an acidic bonding agent, then the reaction temperatures lie generally between -20 DEG C and +100 DEG C, preferably between 0 DEG C and 50 DEG C.

The symmetric carbonic acid anhydrides needed with the method according to invention (C-C2/Variante beta) as reaction components are clearly defined by the formula (VII). In this formula R< has; 9> preferably that meaning, preferably which was already called in connection with the description of the materials according to invention of the formula (I) for this remainder.

The symmetric carbonic acid anhydrides of the formula (VII) are admitted or can after well-known in principle methods in simple way be manufactured.

Preferably as diluents those diluents can be used with the lead-through of the method according to invention (C-C2/Variante beta), preferably which are possible also with the method (C-C2/Variante alpha). In all other respects also a Carbonsäureanhydrid of the formula (VII), used in the surplus, can function simultaneous as diluents.

The reaction temperatures can be varied also with the method according to invention (C-C2/Variante beta) within a larger range. Generally one works at temperatures between -20 DEG C and +150 DEG C, preferably between 0 DEG C and 100 DEG C.

With the lead-through of the according to invention of the method (C-C2/Variante beta) the basic materials of the formulas become (Ib) and (generally VII) in approximated equivalent quantities uses. It is however also possible to use the carbonic acid anhydride in a larger surplus. The working-up takes place after usual methods.

Generally one proceeds in such a way that one removes diluents and in the surplus existing carbonic acid anhydride as well as the developing carboxylic acid by distillation or by washing with an organic solvent or with water.

The asymmetric Säureanhydride needed with the method according to invention (C-C2/Variante gamma) as reaction components are clearly defined by the formula (VIII). In this formula R< has; 9> preferably that meaning, preferably which was already called in connection with the description of the materials according to invention of the formula (I) for this remainder. R preferably stands for alkyl with 1 or 2 carbon atoms or for Phenyl.

The asymmetric Säureanhydride of the formula (VIII) are admitted or can after well-known in principle methods in simple way be manufactured. Thus one receives connections of the formula (VIII) by the fact that one carboxylic acid of the formula

HO-@-R< 9>

in which

R< 9> the meaning indicated above has,
with carbonic acid ester chloride of the formula (XV)

R-O-@-Cl (XV)

in which

R the meaning indicated above has,
in presence of a diluent, like e.g. Dichloromethane, and in presence of an acidic bonding agent, like e.g. Tri-ethylamine, at temperatures between -20 DEG C and +100 DEG C, preferably between 0 DEG C and 50 DEG C, converts.

The asymmetric Säureanhydride of the formula (VIII) are continued to process generally not in pure form insulated, but in the resulting form, if necessary after previous distance by diluent and/or salts.

Preferably as diluents those diluents can be used with the lead-through of the method according to invention (C-C2/Variante gamma), preferably which are possible also with the method (C-C2/Variante alpha). In all other respects used Säureanhydrid of the formula (VIII) can function simultaneous as diluents also in the surplus.

The reaction temperatures can be varied also with the method according to invention (C-C2/Variante gamma) within a larger range. Generally one works at temperatures between -20 DEG C and +150 DEG C, preferably between 0 DEG C and 100 DEG C.

With the lead-through of the according to invention of the method (C-C2/Variante gamma) the basic materials of the formulas become (Ib) and (generally VIII) in approximated equivalent quantities uses. It is however also possible to use the Säureanhydrid in a larger surplus. The working-up takes place after usual methods.

The omega needed as reaction components - halogen carbonic acid halides (method C-C2/Variante delta) are clearly defined by the formula (IX). In this formula R< have; $1 > < 2 > < - > < 1 >$, $R < 1 > < 2 > < - > < 2 >$, $R < 1 > < 2 > < - > < 3 >$, $R < 1 > < 2 > < - > < 4 >$ and R preferably those meanings, preferably which were already called in connection with the description of the materials according to invention of the formula (I) for these remainders. Hal and Hal< 2> preferably stand for chlorine and bromine.

The omega - halogen carbonic acid halides of the formula (IX) are admitted or can after well-known in principle methods in simple way be manufactured.

As acidic bonding agents all usual acidic acceptors come into consideration during the conversion to the method according to invention (C-C2/Variante delta). For the 1. Stage preferably uses one third. Amines, like tri-ethylamine, Pyridin and N, N-Dimethylanilin, furthermore alkali and alkaline earth metal oxides such as sodium carbonate, potassium carbonate and calcium carbonate.

For the 2. Reaction step alkaline-earth hydroxides preferably become such as potassium hydroxide and sodium hydroxide, furthermore alkali or alkaline-earth alcoholates such as Natriummethanolat, Magnesiummethanolat and potassium third. - butylat as well as alkali or alkaline-earth hydrides such as sodium hydride, Kaliumhydrid and calcium hydride uses.

As diluents all Solventien inert opposite Säurehalogeniden and strong bases can be used with the method according to invention (C-C2/Variante delta). Preferably usable hydrocarbons are such as benzene, toluol, xylene and tetralin, further ethers such as diethyl ethers, tetrahydrofurans and Diöxon as well as polar Solventien such as Dimethylsulfoxid, sulfolane, N-Methylpyrrolidon or dimethyl formamide.

With the lead-through of the according to invention of the method (C-C2/Variante delta) the basic materials of the formulas become (Ib) and (generally IX) in approximated equivalent quantities uses. It is however also possible to begin or other component in a larger surplus. The working-up takes place after the usual methods.

The reaction temperatures can be varied with the lead-through of the method according to invention (C-C2/Variante delta) within a larger range. If one works in presence of a diluent and in presence of an acidic bonding agent, then the reaction temperatures lie generally between -78 DEG C and +100 DEG C, preferably between -78 DEG C and +50 DEG C.

The methods according to invention (C-C2/Variante alpha, beta, gamma and delta) are accomplished generally with normal print.

The connections of the formula (IC), needed for the lead-through of the method according to invention (D) as basic materials, materials according to invention are available and after the methods (A), (B) or (C):

In the formula (IC) R< have; $1 >$, $R < 2 >$, $R < 3 >$, $R < 4 >$, $R < 5 > < - > < 1 >$, $R < 6 >$ and X preferably those meanings preferably, which were already called with the description of the materials according to invention of the formula (I) for these substituents, $R < 5 > < - > < 1 >$ stands for the remainder - @@@-R< 9>

, whereby R< 7> and R< 9> preferably for the remainders, preferably which were called with the description of the materials of the formula (I).

As diluents to the lead-through of the method according to invention (D) inert organic solvents infrage come. To it belong in particular aliphatic or aromatic, if necessary halogenated hydrocarbons, as for example to benzine, benzene, toluol, xylene, Chlorbenzol, Petrolether, hexane, cyclohexane, Dichlormethan, chloroform, carbon tetrachloride, ether, like diethyl ethers, Dioxan or tetrahydrofurans.

The reaction temperatures can be varied with the lead-through of the method according to invention (D) within a larger range. Generally one works at temperatures between +20 DEG C and +200 DEG C, preferably between 50 DEG C and 150 DEG C.

The method according to invention (D) is accomplished generally under normal print. It is to be worked however also possible at increased or decreased pressure.

To the lead-through of the method according to invention (D) inserts one per mol at connection of the formula (IC) 0.5 to 5.0 mol, preferably 0.5 to 2.0 mol, at Schwefelungsagentien.

In the connections of the formula (ID), needed with the method according to invention (E) as basic materials, R< are located; $1 >$, $R < 2 >$, $R < 3 >$, $R < 4 >$, $R < 5 > < - > < 2 >$, $R < 6 >$ and X preferably for those meanings, those already with the description of the fabrics according to invention of the formula (I) preferably for these substituents and/or. this index were called. The bonds of the formula (ID) are available bonds according to invention and after method (D).

The connections needed with the method according to invention (E) further as basic materials are defined by the formula (X) general. In the formula (X) R< has; $1 > < 1 >$ preferably that meaning, preferably which was already called with the description of the materials according to invention of the formula (I) for this substituent. L preferably stands for chlorine, bromine, Methylsulfonyloxy, Ethylsulfonyloxy or Phenylsulfonyloxy.

The connections of the formula (X) are general well-known connections of organic chemistry.

As deprotonierende bases to the lead-through of the method according to invention (E) all usual bases infrage usable for

such reactions come.

Preferably one uses alkali alcoholates as for example potassium third. - butylat, Natriummethylat, Natriumbutylat, sodium or potassium hydroxide, potassium carbonate, sodium or Lithiumhydrid.

As diluents to the lead-through of the method according to invention (E) inert organic solvents infrage come. Preferably one uses alcohols as for example third. - Butanol, ethanol, isopropanol, dimethyl formamide, N-Methylpyrrolidon, Dimethylsulfoxid, sulfolane, tetrahydrofuran or Dioxan.

The reaction temperatures can be varied with the lead-through of the method according to invention within a larger range. Generally one works at temperatures between 0 DEG C and 200 DEG C, preferably at 20 DEG C to 120 DEG C.

The method according to invention (E) is accomplished generally with normal print. It is however also possible to work at increased or decreased pressure.

In the connections of the formula (If), needed with the method according to invention (F) as basic materials, R< are located; 1>, R< 2>, R< 3>, R< 4>, R< 6> and X preferably for those meanings, preferably which were already called with the description materials according to invention of the formula (I) for these substituents. R< 5> < - > < 3> (A) stands for Hydroxy, bonds of the formula (If) is available bonds according to invention and after methods.

The connections needed with the method according to invention (F) further as basic materials are defined by the formula (XI) general. In the formula (XI) R< has; 5> < - > < 4> preferably that meaning, preferably which was already called with the description of the materials of the formula (I) for the appropriate substituents. G preferably stands for chlorine, bromine, Methylsulfonyloxy, Phenylsulfonyloxy or Tylsulfonyloxy.

The bonds of the general formula (XI) are admitted or can after well-known in principle methods in simple way be manufactured (see. e.g. Helv. Chim. Acta 63 1412 (1980)).

As diluents all inert Solventien can be used with the method according to invention (F). Preferably usable halogen hydrocarbons, like dichloromethane, are chloroform, carbon tetrachloride, Chlorbenzol and o-Dichlorbenzol and hydrocarbons such as toluol, xylene and tetralin, further cyclische ethers, like tetrahydrofurans and Dioxan, beyond that esters of carboxylic acid, like ethyl acetate and Glykolmonomethyletheracetat and also strongly polar Solventien, like Dimethylsulfoxid, sulfolane, N-Methylpyrrolidon, Dimethylacetamid and dimethyl formamide.

As acidic bonding agents all usual acidic acceptors come into consideration during the conversion to the method according to invention (F). Tertiary amines, like tri-ethylamine, are preferably usable Pyridin and N, N-The methyl-anilin, furthermore alkaline earth metal oxides, like magnesium and calcium oxide, in addition alkali and alkaline earth metal carbonates, like sodium carbonate, potassium carbonate and calcium carbonate, in addition alkali and alkaline earth metal hydroxides, like lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide, alkali and alkaline-earth alcoholates such as Natriummethylat, Natriumethylat, potassium third. - butylat and Magnesiumethylat, alkali and alkaline-earth hydrides such as sodium hydride, Kaliumhydrid and calcium hydride.

The reaction temperatures can be varied with the lead-through of the method according to invention (F) within a larger range. Generally one works at temperatures between -20 DEG C and +250 DEG C, preferably between 50 DEG C and 200 DEG C.

With the lead-through of the method according to invention (F) the basic materials of the formulas become (If) and (XI) and also if necessary the cousin generally approximated in equivalent quantities used. However also possible or other reaction component is to be used in a larger surplus. The working-up takes place after usual methods.

The active substances according to invention can be used as Defoliant, Desiccant, herb killing means and in particular as weed killers. By weed in the broadest sense all plants are to be understood, which grow up at places, where they are unwanted. Whether the materials according to invention work as total or selective herbicides, essentially depends on the applied quantity.

The active substances according to invention can e.g. with the following plants to be used:

Dikotyle of weeds of the kinds:

Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Centaurea.

Dikotyle cultures of the kinds:

Gossypium, glycines, beta, Daucus, Phaseolus, Pisum, Solanum, Linum, Ipomoea, Vicia, Nicotiana, Lycopersicon, Arachis, Brassica, Lactuca, Cucumis, Cucurbita.

Monokotyle of weeds of the kinds:

Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Spheoclea, Dactyloctenium, Agrostis, Alopecurus, Apera.

Monokotyle cultures of the kinds:

Oryza, Zea, Triticum, Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, pineapple, Asparagus, Allium.

The use of the active substances according to invention is limited however by no means to these kinds, but extends same way also to other plants.

The connections are e.g. suitable as a function of the concentration for the total weed control. on industrie and trackages and at ways and places with and without tree vegetation. Just as the connections can to the weed control in continuous cultures, e.g. Forest, ornamental shrub, fruit, wine, Citrus, nut, banana, coffee, dte, rubber, Ölpalm, cocoa, potato berry

and hop lay close and to the selective weed control in one year's cultures to be used.

The active substances according to invention with particularly good success can be begun for selective fight mono and dikotyler weeds in particular in monokotylen cultures in the NAK accumulating up run procedure.

In addition the active substances according to invention show an grow-adjusting effect and can as Defoliantmittel be used.

The active substances can be transferred into the usual formulations, like solutions, emulsions, spraying powders, suspensions, powders, types of dust means, pastes, soluble powders, granular materials, suspension emulsion concentrates, active substance-impregnated nature and synthetic materials as well as purifying encapsulations in polymere materials.

These formulations are manufactured in well-known way, z. B. by mixing the active substances with diluents, thus liquid solvents and/or solid carrier materials, if necessary using surface-active compositions, thus emulsifiers and/or dispersing agents and/or foam-producing compositions.

In case of the use of water as diluents can e.g. also organic solvents as auxiliary solvents to be used. As liquid solvents are essentially applicable: Aromatics, like xylene, toluol, or alkyl naphtha LINE, chlorinated aromatics and chlorinated aliphatic hydrocarbons, like chlorine benzene, Chlorethylene or dichloromethane, aliphatic hydrocarbons, like cyclohexane or paraffins, e.g. Erdölfraktionen, mineral and vegetable oils, alcohols, like Butanol or glycol as well as their ether and ester, vinyl ketones such as acetone, methyl-ethyl ketone, Methylisobutylketon or cyclohexanone, strongly polar solvents, like dimethyl formamides and Dimethylsulfoxid, as well as water.

As solid carrier materials are applicable: E.G. Ammonium salts and natural powdered minerals, like Kaoline, aluminas, talcum powder, chalk, quartz, Attapulgit, Montmorillonit or Diatomeenerde and synthetic powdered minerals, like hochdisperse silicic acid, aluminium oxide and silicates, as solid carrier materials for granular materials are applicable: e.g. broken and fractionated natural rocks such as Calcit, marble, pumice, Sepiolith, dolomite as well as synthetic granular materials from inorganic and organic flours as well as granular materials from organic material such as Sägemehl, coconut bowls, ears of corn and tobacco stacks; as emulsify and/or foam-producing compositions are applicable: e.g. nichtionogene und anionische Emulgatoren, wie Polyoxyethylen-Fettsäure-Ester, Polyoxyethylen-Fettalkohol-Ether, z.B. Alkylaryl-polyglykolether, Alkylsulfonate, Alkylsulfate, Arylsulfonate sowie Eiweißhydrolysate; as dispersing agents are applicable: e.g. Lignin Sulfitablaugen and methyl cellulose.

Bonding agents can be used such as carboxymethylcellulose, natural and synthetic pulvrige, granular or latexförmige polymers, like Gummiarabicum, polyvinyl alcohol, polyvinyl acetate in the formulations, as well as natural Phospholipide, like Kephalline and Lecithine and synthetic Phospholipide, further additives can be mineral and vegetable oils.

Dyes can do like inorganic pigments, e.g. Iron oxide, titanium oxide, ferrous cyan blue and organic dyes, like alizarine, Azo and Metallphthalocyaninfarbstoffe and trace nutrients such as salts by iron, manganese, boron, copper, cobalt, molybdenum and zinc to be used.

The formulations contain generally between 0,1 and 95 weight percentage active substance, preferably between 0,5 and 90%.

The active substances according to invention can find as such or in their formulations also in mixture with well-known herbicides to the weed control use, whereby finished formulations or tank mixtures are possible.

For the mixtures well-known herbicides come like e.g. 1-Amino-6-ethylthio-3 (2,2-dimethylpropyl) - 1,3,5-triazin-2,4 (1H, 3H) - dion or n (2-Benzthiazolyl) - N, N min - dimethyl urea to the weed control in grain; 4-Amino-3-methyl-6-phenyl-1,2,4-triazin-5 (4H) - on to the weed control in sugar beets and 4-Amino-6 (1,1-dimethylethyl) - 3-methylthio-1,2,4-triazin-5 (4H) - on to the weed control in soybeans, in question.

Also mixtures with Aryloxyalkansäuren such as 2,4D; 2,4DP; 2,4DB; MCPA; MCPP or Triclopyr; Aryloxy more phenoxyalkansäureester like Diclofop methyl, Fenoxaprop, (2R) - 2 [4 (3,5-Dichlor-pyridyl-2-oxy) - phenoxy] - prop. ion outer RH (trimethylsilyl) - methylester; Aryl carbonic acids such as Dichlorpicolinsäure; Diphenylether such as Bifenox; Ureas such as Chlortoluron, Fluometuron, Isoproturon, Methabenzthiazuron; Imidazolinone such as Imazamethabenz; Nitriles such as Bromoxynil or Ioxynil; Oxyacetamide such as Mefenacet; Sulphonylureas such as Chlorsulfuron, Thiameturon; Thiocarbamate such as Triallate, Triazindione such as Amethydione; Triazine such as Terbutryne, Triazinone such as Ethozin or metribuzins as well as Bentazone come infrage. Some mixtures show surprisingly also synergistic effect.

Also a mixture with other well-known active substances, like fungicides, insecticides, Akariziden, Nematiziden, protective agents bird-ate approximately, from plant nutrients and soil structure improvement means is possible.

The active substances can be used as such, in form of their formulations or the application forms, like ready for use solutions, prepared from it by further diluting, suspensions, emulsions, powders, pastes and granular materials. The use happens in usual way, e.g. by pouring, syringes, spraying, strewing.

The active substances according to invention can be appliziert both before and after accumulating the plants.

They can be trained also before the seed into the tray.

The applied active substance quantity can vary within a larger range. It essentially depends on the kind of the desired effect. Generally the expenditure quantities lie between 0,01 and 10 kg active substance per hectare of floor space, preferably between 0,05 and 5 kg per hectare.

The making and the use of the active substances according to invention come out from the following examples.

Manufacture examples

Example I-1 (method A)

2 (4-Neopentyloxyphenylthio) - 4-methylamino-6-methylpyrimidin
EMI67.1

3.53 g (20 mMol) 4-Neopentyloxy-thiophenol are submitted to powdered potassium hydroxide in 20 ml N-Methylpyrrolidon under nitrogen atmosphere and shifted with 1,23 g (22 mMol). After 15 minutes 3.62 g (20 mMol) are added 4-N-Methylamino-6-methyl-2-methylsulfonylpyrimidin and to 2 hours to 120 DEG C are warmed up. The reaction mixture is stirred into 150 ml 1N sodium hydroxide solution, the precipitation is sucked off and dried. By recrystallizing from toluol/n-hexane one receives 2 (4-Neopentyloxyphenylthio) - 4-methylamino-6-methylpyrimidin to 4.63 g (81%) from the melting point 104 DEG C.

Example I-2 (method B)

2 (4-Nitrophenylthio) - 4-amino-6-methylpyrimidin
EMI67.2

28.2 g (0.1 mol) 2 (4-Nitro-phenylthio) - 4-chlor-6-methyl-pyrimidin are shifted in 200 ml Dioxan in a VA-Druckautoklaven with 5,1 g (0.3 mol) liquid ammonia. The mixture becomes 5 hours on 120 to 125 DEG C heated (internal pressure up to 37 bar). After easing the solvent is abdestilliert to a large extent, the residue is stirred into 1 litre water. The failed product is sucked off, washed with water and dried at air. One receives 2 (4-Nitro-phenylthio) - 4-amino-6-methyl-pyrimidin to about 25 g (95% of the theory) from the melting point 175 to 177 DEG C (from Butanol recrystallizes).

Example I-3 (method B)

2 (4-Nitrophenylthio) - 4-methylamino-6-methylpyrimidin
EMI68.1

28.2 g (0.1 mol) 2 (4-Nitro-phenylthio) - 4-chlor-6-methyl-pyrimidin are solved in 200 ml Dioxan. Into this solution one leads gaseous methylamine in the surplus under agitating at first at ambient temperature, then with up to 75 DEG C of rising temperature (approx. 10 g SIMILAR 0.3 mol). If by dünnenschichtchromatographischen proof the Vorprodukt is completely converted, one evaporates the solvent in the vacuum to a large extent and mixes the residue with water. The solid product is sucked off, washed with water and dried at air. One wins 25.8 g (93.5% of the theory) 2 (4-Nitrophenylthio) - 4-methylamino-6-methyl-pyrimidin of the melting point Fp: 130 DEG C to 132 DEG C (from tetrachloromethane recrystallizes).

Example I-4 (method C-C1)

2 (4-Aminophenylthio) - 4-amino-6-methylpyrimidin
EMI69.1

26.2 g (0.2 mol) 2 (4-Nitro-phenylthio) - 4-amino-6-methyl-pyrimidin are solved in 250 ml Dioxan and hydrogenated after addition from 3 g Raney nickel in a VA-Druckautoklaven up to the saturation (4 hours). The temperature up to 55 DEG C rises. After easing autoclaves the catalyst is filtered off, the solution in the vacuum is evaporated. One receives 2 (4-Amino-phenylthio) - 4-amino-6-methyl-pyrimidin to 22.5 g (97% of the theory) from the melting point Fp. 176 DEG C to 178 DEG C (from Butanol recrystallizes).

Example I-5 (method C-C2/Variante alpha)

2 (4-Pivaloylamino-phenylthio) 4-amino-6-methylpyrimidin
EMI70.1

23.2 g (0.1 mol) 2 (4-Amino-phenylthio) - 4-amino-6-methyl-pyrimidin are solved in 200 ml tetrahydrofurans. Hierzu gibt man 10,1 g (0,1 Mol) Triethylamin und tropft anschliessend unter schwacher Kühlung bei 15 DEG C bis 20 DEG C 12,05 g (0,1 Mol) Pivalsäurechlorid zu. The mixture is after-agitated still 3 hours at ambient temperature, evaporated in the vacuum and mixed the residue with 1 litre water. The separated crystals are sucked off, washed with water and dried at air. One receives 2 (4-Pivaloylamino-phenylthio) - 4-amino-6-methyl-pyrimidin to 29 g (91.7% of the theory) from the melting point Fp: 182 DEG C to 184 DEG C. After findings < 1> H-NMR remains the 4-Aminogruppe in the Pyrimidinring under these conditions invariably.

Example I-6 (method C-C2/Variante delta)
EMI70.2

23.2 g (0.1 mol) 4 (4-Amino-6-methyl-2-pyrimidylthio) - aniline are solved in 300 ml absolute tetrahydrofuran and shifted with 10,2 ml (0.1 mol) absolute Pyridin. With 0 DEG C to 10 DEG C 21.11 g (0.105 mol) are course-dripped 4-Chlor-2,2-dimethyl-buttersäurechlorid and afterwards 30 minutes at ambient temperature are agitated. After sucking the hydrochloride off one confines the filtrate on approx. ml and this quick to a suspension from 12,33 g (0.11 mol) potassium third gives 100. - butylat in 80 ml absolute tetrahydrofuran, which is precooled on -70 DEG C. The mixture is stirred into 1 litre ice water, which recrystallizes precipitation sucked off, dried and from chloroform/n-hexane. One receives 13.72 g (41.8% of the theory) of the above-mentioned pyrrolidone from the melting point 208 DEG C.

In appropriate way and in accordance with the general data to the making one receives the Aryloxy specified in the following table (and/or. thio) aminopyrimidine of the formula (I) EMI71.1 EMI72.1 EMI73.1 EMI74.1 EMI75.1 EMI76.1 EMI77.1 EMI78.1 EMI79.1 EMI80.1 EMI81.1 EMI82.1 EMI83.1 EMI84.1 EMI85.1 EMI86.1

Vorprodukte

Example IIIa-1

4 (3,3, - Dimethylbutyl) - thiophenol
EMI87.1

7.5 g (0.2 mol) are submitted to sodium boron hydride in 140 ml Diethylenglykoldimethylether and course-dripped with

30 - 40 DEG C a solution of 41,6 g (0.2 mol) 4 (3,3-Dimethylbutyro) - thiophenol in 60 ml Diethylen glykoldimethylether. One lets 2 hours after-react with 120 DEG C, admits under ice cooling 100 ml to water, places with 20% to iger sulphuric acid more acidic and adds again to 200 ml water. The reaction mixture is extracted now with 250 ml dichloromethane, which distills organic phase with 250 ml water out-vibrated, over magnesium sulfate dried and over an annular gap column. One receives 23 g (60% D. Th.) 4 (3,3-Dimethylbutyl) - thiophenol of the boiling point 98 DEG C/0,4 mbar.

Example IIIb-1 (Vorprodukt of example IIIa-1)

4 (3,3-Diemthylbutyro) - thiophenol
EMI87.2

Are submitted to 18.5 g (0.2 mol) Natriumhydrogensulfid in 100 ml N-Methylpyrrolidon and drained by Andestillieren with xylene. One leaves on 140 DEG C cooling, gives to 21.05 g (0.1 mol) 4 (3,3-Dimethylbutyro) - chlorbenzol in addition, lets 3 hours after-react with 160 DEG C and distills the N-Methylpyrrolidon off. The residue is taken up, filtered to 1 litre water and acidified the filtrate with 0 10 DEG C with halfconcentrated hydrochloric acid. The precipitation is sucked off, washed and dried neutral. After distillation of the mother liquor under decreased pressure one receives 4 (3,3-Diemthylbutyro) to 14 g (70% of the theory) - thiophenol by the boiling point: 110 -115 DEG C/0,1 mbar.

Example XIV-1

2 (4-Nitrophenylthio) - 4-hydroxy-6-methylpyrimidin
EMI88.1

28.4 g (0.2 mol) 2-Thio-4-hydroxy-6-methylpyrimidin are suspended in 160 ml sulfolane. For this one gives pulverized potassium hydroxide 22.4 by portion to g (0.4 mol) at ambient temperature under agitating. One agitates 30 minutes after and admits afterwards 31.5 to g (0.2 mol) 4-Chlor-nitro-benzol. The mixture is cooled down 3 hours on 50 DEG C, then 3 hours on 120 DEG C heated, and stirred into 2 litres water. After addition of 25 ml konz. Potassium hydroxide solution is filtered the solution by insoluble components and acidified afterwards with diluted hydrochloric acid. The precipitation is sucked off, washed with water neutral and dried with 80 DEG C to 90 DEG C. One receives 2 (4-Nitrophenylthio) - 4-hydroxy-6-methylpyrimidin to 42.6 g (81% of the theory) from the melting point Fp: 238 DEG C to 240 DEG C (from Glykolmonomethylether recrystallizes).

In analog way one wins:

Example XIV-2:

2 (2-Methoxy-4-nitro-phenylthio) - 4-hydroxy-6-methylpyrimidin; Fp: 256 DEG C to 258 DEG C (from dimethyl formamides).

Example XIV-3:

2 (2-Methyl-4-nitro-phenylthio) - 4-hydroxy-6-methyl-pyrimidin; Fp: 212 DEG C to 214 DEG C.

Example IV-1

2 (4-Nitrophenylthio) - 4-chlor-6-methylpyrimidin
EMI90.1

52.6 g (0.2 mol) 2 (4-Nitro-phenylmercapto) - 4-hydroxy-6-methyl-pyrimidin are suspended in 250 ml Phosphoroxchlorid. The mixture is cooked under agitating gradually for simmering heated and at the return flow, until the hydrogen chloride development terminated and a clear solution developed. Surplus Phosphoroxchlorid is abdestilliert in the vacuum, the residue is registered into 2 litres ice water. The separated product is sucked off, washed with water and dried at air. After recrystallizing from petroleum ether one receives 2 (4-Nitro-phenylthio) - 4-chlor-6-methylpyrimidin to 12 g (21.3% of the theory) from the melting point Fp: 132 DEG C to 134 DEG C.

In analog way one manufactures:

Example IV-2:

2 (2-Methoxy-4-nitro-phenylthio) - 4-chlor-6-methylpyrimidin; Fp: 140 DEG C to 141 DEG C.

Example IV-3:

2 (2-Methyl-4-nitro-phenylthio) - 4-chlor-6-methylpyrimidin; Fp: 118 DEG C to 119 DEG C.

Example of use

In the following example of use those was used below specified connection as Vergleichssubstanz: EMI92.1 2 (3-Chlorphenoxy) - 4-dimethylaminopyrimidin (admits 28 from EP-A 1187/Beispiel)

Example A

Post office emergence test

Solvent: 5 parts by weight acetone

Emulsifying agent: 1 part by weight Alkylaryl polyglykolether

To the making of an appropriate active substance preparation one mixes 1 part by weight active substance with the indicated quantity of solvent, admits the indicated quantity emulsifying agent and dilutes the concentrate with water on the desired concentration.

With the active substance preparation one squirts Testplanzen, which a height of 5 - 15 cm have so that the active substance quantities per unit area, wished in each case, become discharged. The concentration of the Spritzbrühe is selected in such a way that in 2000 l Wasser/ha become the active substance quantities of discharged wished in each

case. After three weeks the damage degree of the plants bonitiert in % damage in the comparison to the development the unbe acted control.

Mean:

0% = no effect (like untreated control)

100% = total destruction

A clear superiority in the useful plant selectivity as for example with wheat and in herbicides the effect against mono and dikotyle weeds as for example Amaranthus, Chenopodium, Galinsoga, Sinapis and Setaria opposite the Vergleichssubstanz (A) e.g. show. In accordance with connections the manufacture examples: 1, 5, 6, 11, 20, 27, 29, 30, 31, 32, 36, 56 and 59.